REQ. NO. 0-9115

The Final Report of the Project On

CONTRACT REPORT NO. OSU80-00237

DEGRADATION OF COKE IN THE BLAST FURNACE

DSS File No. 05SU.23440-0-9115
Contract Serial No. OSU80-00237

to be submitted to

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March, 1982

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SUMMARY (1979-1981)

The ambitious goal of relating properties of coal and conditions of carbonization to properties of coke and blast furnace performance has been partly reached through the work of many research workers in the past years. The empirical relationships between characteristics of coals from major deposits and carbonization conditions and the physical properties of coke are found to be adequate for the need of the steel industry at the present time. The corelations between coke properties and blast furnace performance are still very poor. It appears that the lack of proper characterization of the chemical properties of coke and the complexity of blast furnace reactions are the main drawbacks for progress in this direction.

The reactivity test (with carbon dioxide) and the recently developed "after reaction strength" test contribute to better understanding of the behavior of blast furnaces in Japan. However, it cannot explain many disasters in North America due to excessive degradation of coke inside the blast furnace. There is evidence that high alkalies circulation was at least one of the causes of the problem. It is the personal opinion of the writer that the difference in the severity of alkalies related problems in blast furnace operations in Japan and in Canada, is not related to the amount of alkalies in the raw materials. It is the stable operational conditions in Japan which prevent favorable conditions for alkalies attack on coke.

This project was designed to carry out the pioneer work on coke degradation inside blast furnaces caused by alkalies. For the three phases of work, the subjects of investigation and major conclusions are outlined below.

1. (1979) The degradation of coke caused by potassium vapor in the absence of carbon dioxide was studied. The pronounced effect can be explained by the formation of intercalation compound of carbon and potassium with a volume expansion[1]. The adverse effect is more severe at temperatures (below 1000°C) prevailing in the stack region of the blast furnace. Under certain conditions a larger gradient of potassium would form in a coke lump (i.e., a larger stress due to differential volume expansion). The larger the gradient the lower the strength of coke will be. Such conclusion has been confirmed in the

blast furnaces of Kawasaki Steel Corporation, as learned through private communications.

2. (1980) The degradation of coke caused by carbon dioxide and the catalytic effect of potassium were investigated. The Brazilian method for brittle materials was used to measure the tensile strength of specimens cut from commercial coke. For the specimens studied in this project, the lowering of the tensile strength of commercial coke is related to the degree of gasification of carbon, irrespective of the conditions under which gasification of carbon by CO_2 actually took place. Potassium absorbed by carbon in coke has accelerated the oxidation reaction under all conditions studied. The most important change in the kinetics is the lowering of the minimum temperature at which CO_2 can gasify carbon at a measurable reaction rate. The effect of alkalies in blast furnace gas makes the conventional reactivity tests irrelevant to blast furnace operations. The results mentioned above have been presented at the AIME Annual Meeting, February, 1981[2].
3. (1981) The mechanisms of the weakening of coke as the result of attack by carbon dioxide and/or potassium vapor were studied. The degradation of coke at lower temperatures is essentially due to the formation of intercalation compounds because the gasification by CO_2 is negligibly slow below a critical temperature. On the other extreme, when the gasification of carbon was over about 20% the influence of potassium in the specimen became insignificant. There is strong evidence that gas/carbon reactions did not take place uniformly on the external surface of the specimens. A preliminary work of quantitative microscopy was carried out and a "Relative Micro Reactivity" index defined. Our work has shown that the texture of carbon in coke appears to be the missing link between the characterization and the prediction of chemical properties of coke. It has been published in 1981[3].

Final Report

DEGRADATION OF COKE IN THE BLAST FURNACE - PHASE III

January 1 - December 31, 1981

1. Objectives Stated in the Original Proposal

The ensurance of quality of coke in the form of meeting a minimum value in stability index is necessary but not sufficient. The degradation of coke in the blast furnace which is not because of low stability can only be attributed to chemical attack by carbon dioxide and by alkali vapors, etc. The conventional "Reactivity Tests" have been proven to be essentially irrelevant. This research contract was aimed at discovering certain relationships between the resistance of coke against the degradation due to chemical attack by carbon dioxide and alkalies on one hand and characteristics of coke and conditions under which reactions take place, on the other.

2. The Strategy of Experimental Design

Based on the temperature at which coke degrades inside a blast furnace, the following four mechanisms and related tests may be classified:

a) Near ambient temperature:-
   The breakage due to impact and abrasion is measured by stability tests.

b) Below the temperature at which the solution loss reaction becomes significant (i.e., < 900°C):-
   The breakage due to the formation of intercalaction compound with alkali vapors, the subject of investigation of the first two years of the project.

c) The temperature range in which the solution loss reaction is active (i.e., 900 < and < 1200°C):-
   The weakening of coke due to increased porosity and thinned pore walls, with and without catalytic effect, was part of the subject of investigation in the second year.

d) High temperature degradation:-
   The weakening of coke due to carbon-ash reactions and uneven shrinkage.

3. Results

A. Strength of Coke and Degree of Gasification

The specimens in the form of discs were cut from a commercial blast furnace coke of about 60 stability and 8% ash. Discs with or without prior impregnation of potassium were oxidized to various degrees of burning-off (in percent of weight loss of the specimen) and then followed by tensile strength measurement at room temperature.

Catalytic Effect of Potassium on Carbon Oxidation

The catalytic effect of potassium on the oxidation of carbon at 1000°C is shown in Figure 1. The bottom line represents an extensive experimentation with the coke without impregnation of potassium. The results at 800 and 1200°C as a function of potassium contents are shown in Figures 2 and 3. The extremely strong effect at 800°C (without impregnation the rate was nil) suggests that it could have an important impact on blast furnace operations by lowering the thermal reserve zone temperature and the extent of indirect reduction. At higher temperatures the diffusion of gases would have a dominant role in the kinetics. However, as shown in Figure 3, the influence of the potassium content in coke is very obvious.

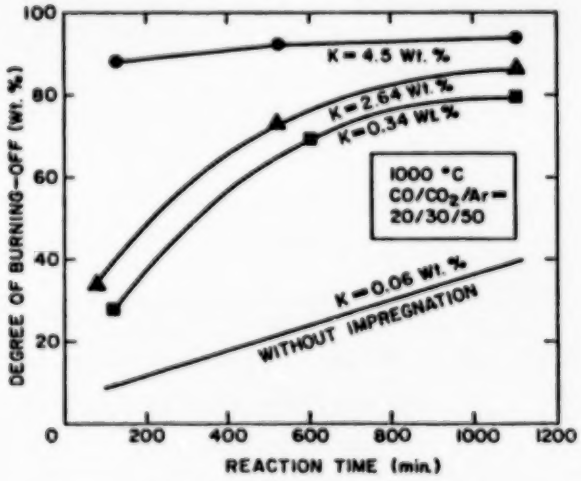

Fig. 1. The effect of potassium content on the kinetics of carbon oxidation at 1000°C.

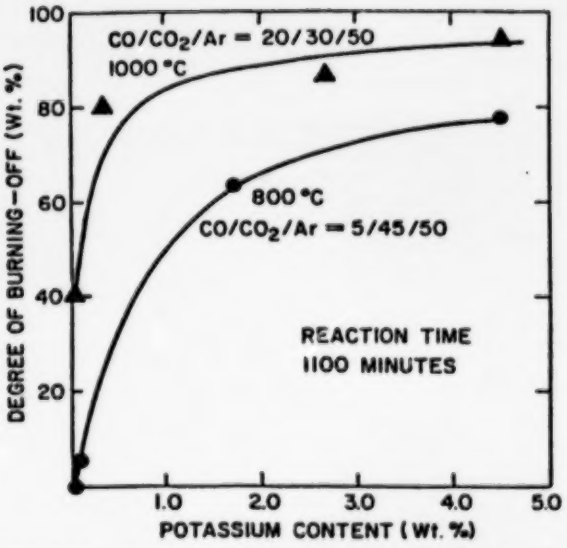

Fig. 2. The effect of potassium content on the kinetics of carbon oxidation at 800 and 1000°C.

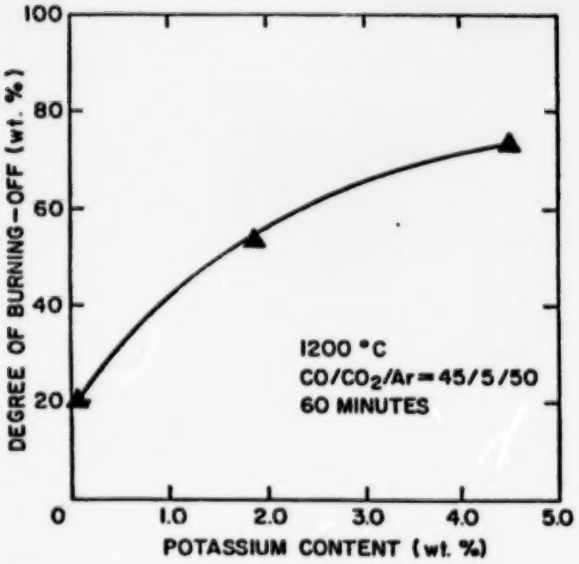

Fig. 3. The effect of potassium content on the kinetics of carbon oxidation at 1200°C.

Strength of Coke and the Degree of Gasification

The tensile strength of partially oxidized discs, without prior impregnation of potassium, was measured. Specimens which suffered different degrees of burning off by varying temperatures, time and composition of oxidizing gas, were used. In Figures 4 and 5, results with the oxidation temperature of 1000 and 1200°C, respectively, are shown. These two sets of data are indistinguisable statistically. One may reach the conclusion that the extent of the loss of strength due to solution loss reaction mainly depends on the degree of burning-off, at least under the conditions investigated in the present work. A single curve represents data in Figures 6 and 7 and will be used as the reference for the illustration of the contribution of absorbed potassium prior to oxidation.

Alkalies Absorption and Oxidation of Carbon

The effects of potassium content, prior to oxidation experiments on mechanical strength of the partially oxidized specimens at room temperature, are shown in Figures 6 and 7. For data shown in both figures the oxidation temperature was 1000°C for all experiments.

In Figure 6, the dotted line represents data in Figures 4 and 5 and the results with specimens of 0.34%K, which are not shown here. The solid

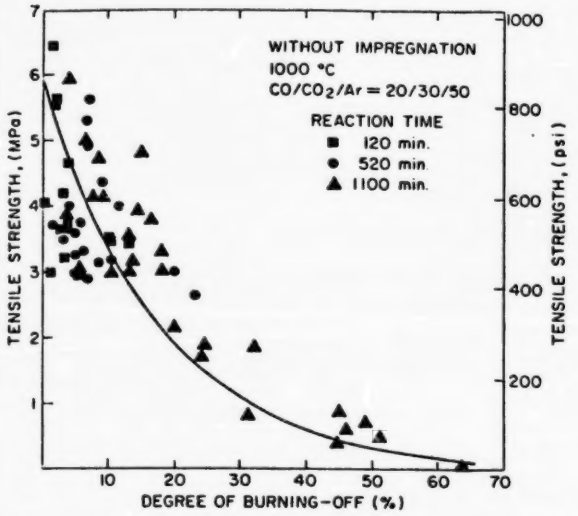

Fig. 4. The reduction of tensile strength of coke discs due to partial oxidation of carbon at 1000°C.

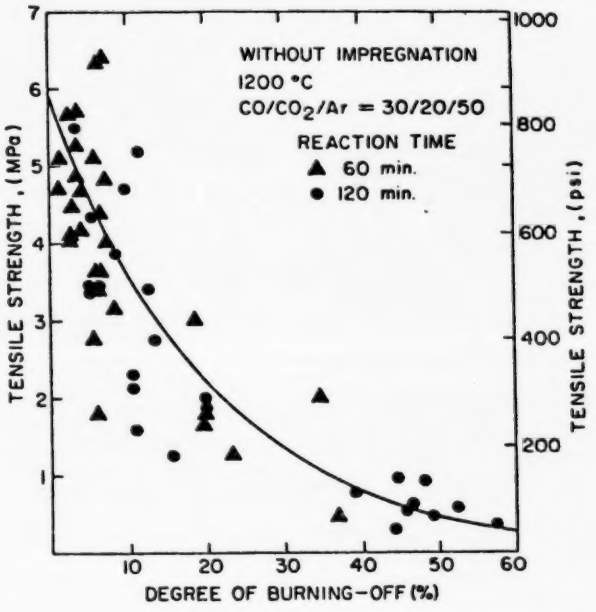

Fig. 5. The reduction of tensile strength of coke discs due to partial oxidation of carbon at 1200°C.

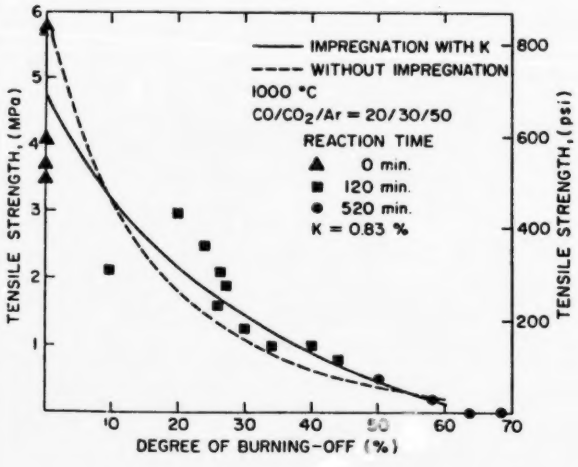

Fig. 6. The reduction of tensile strength of coke discs due to potassium absorption and partial oxidation.

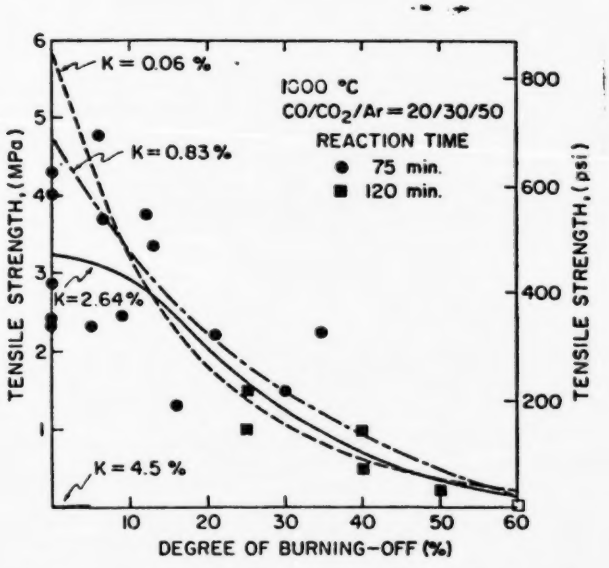

Fig. 7. The reduction of tensile strength of coke discs due to larger amount of potassium absorption and partial oxidation.

curve represents specimens with 0.83% K. These two curves become indistinguishable after 20% burning-off.

The effect of potassium on the loss of tensile strength due to partial oxidation becomes more evident with specimens of medium potassium content (2.64% wt.) but only for a lower degree of burning-off; see Figure 7. For specimens that suffered more than 20% burning-off, under conditions shown in Figures 6 and 7, the relationship of tensile strength vs. degree of burning-off are essentially the same, as long as the potassium content was 2.64% or lower before oxidation. With 4.5% potassium the specimens might remain in one piece. Before and after oxidation, however, they were too weak to obtain any readings for their tensile strength by the present technique. If it is desirable to apply the results shown in Figure 7 to a commercial blast furnace, one may conclude that a moderate cycling of potassium (about ten-fold increase in potassium content in coke in lower stack) would cause coke to degrade more in the lumpy zone, but not necessarily in the coke active region below the melting front.

B. Optical Texture and Reactions

The structure analysis of coke samples taken from various locations in a quenched blast furnace was reported in 1977[4]. With the aid of a series of experiments under controlled conditions (1200°C, pure CO_2 and samples were 10 mm cubes) in the laboratory, Kojima et al. reported that the oxidation of carbon by CO_2 is selective. Their suggestions are further substantiated by the work with cokes made from single coals in the laboratory[5]. Hatano et al. analyzed the optical anisotropy of four kinds of coke samples, which were taken before charging and at tuyeres and that were partially oxidized in the laboratory with or without prior potassium impregnation[6, 7]. The selective nature of carbon oxidation has been confirmed, particularly the difference between the carbon originated from coking or non-coking coals. The fact that coarse mosaic texture is the most resistant against CO_2 attack was the common conclusion in these papers. In the preparation of the partially oxidized specimens in the laboratory, reaction was carried out in the temperature range from 1000 - 1200°C. They failed to notice the influence of potassium (the amount in the sample was reported) on the selectively of carbon oxidation.

Experimental Design

Three types of specimens were used, i.e., the commercial coke and laboratory cokes made from major components (the high volatile and the low volatile coals) of the commercial blend.

The selectivity of oxidation of carbon of various optical textures reflects that the microscopic structure of the solid reactant has a strong influence on the over kinetics of oxidation. In order to observe the effects of the property of solids, the overall reaction should be carried out under the condition that interfacial chemical reaction is a major rate-controlling step. In the present work, the temperature of oxidation was kept at a low-practical temperature; 950 and 850°C (for the sample with prior impregnation of potassium). The composition of the gas was $Ar/CO/CO_2$ = 50/5/45. It is not obvious whether reaction rates under such conditions were in fact controlled by the interfacial reactions, but it should be much closer to the desirable situation than work reported in the literature.

The powder specimens were thinly spread on a screen for uniform gas/

solid contact, so that the degree of burning-off was essentially the same for all particles to be examined under the microscope.

Microscopic Analysis

All the coke samples (approximately 0.5 gr each) remaining from each gasification test were mixed thoroughly with epofix resin in a short plastiglass tube (1.9 cm I.D.). After curing, the coke surface was ground using an abrasive paper 200, 400, 600 and 800 grit. Finally, the specimen was polished with 0.3 micron alumina slurry. The samples were analyzed under the optical microscope using polarized light, a sensitive tint plate and an oil immersion objective given overall magnification of 800 times.

The types of carbon present in the texture were divided following the classification adopted by the Britis- Coke Research Association[8]. The optically identifiable constituents of the wall structure can be summarized as follows:

Isotropic

Mosiac: Fine = Mean grain size = 0.3 μm
Medium = Mean grain size = 0.7 μm
Coarse = Mean grain size = 1.3 μm

Granular Flow

Flow type = Flat
Creased

After counting the type of carbon in each corner of a square field, the sample was displaced 0.2 mm; this process was repeated until 1000 counts were recorded. For each count, an area of 100 μm^2 was assessed. The results are essentially stabilized at 400 counts.

"Relative Micro Reactivity" (RMR)

It must be emphasized that to compare the two states of a widely different degree of burning-off is difficult to arrive at a quantitative result. The rate of diminishing every reactive species is a function of the reactivity as well as quantity of each type of carbon coexistent at any given moment.

The degree of burning-off in the present work was aimed at about 20%, which is less than the most reactive species. The experimental conditions and results are given in Tables I to III.

Table I

Analysis of Optical Anisotopy of a Commercial Coke

	% B.O.	Isotropic	Mosaic Fine	Mosaic Medium	Mosaic Coarse	Mosaic Total	Granular Flow	Flow Type Creased	Flow Type Flat	Flow Type Total
a) Before Impregnation		18.2	20.5	42.0	7.3	69.8	8.6	3.1	0.3	3.4
W (gr. of C)		16.8	19.0	38.9	6.8	64.7	8.0	2.9	0.3	3.2
b) After Gasification	18.65	12.4	13.4	54.3	10.6	78.4	5.6	3.6	--	3.6
Carbon (gr)		9.2	9.9	40.1	7.8	57.8	4.1	2.7	---	2.7
ΔW=(W-Carbon)		7.6	9.1	−1.2	−1.0	6.9	3.9	0.2	0.3	0.5
$A=(\Delta W/W)$ (%)		45.2	47.9			10.7	48.8	6.9	100.0	15.6
A/% B.O. = RMR		2.4	2.6			0.6	2.6	0.4	5.4	0.8
c) After Impregnation and Gasification	33.4	10.5	13.0	56.9	10.8	80.7	5.4	3.1	0.3	3.4
Carbon (gr)		6.2	7.7	33.6	6.4	47.7	3.2	1.8	0.2	2.0
ΔW=(W-Carbon)		10.6	11.3	5.3	0.4	17.0	4.8	1.1	0.1	1.2
$A=(\Delta W/W)$ (%)		63.1	59.5	13.6	5.9	26.3	60.0	37.9	33.3	37.5
A/% B.O. = RMR		1.9	1.8	0.4	0.2	0.8	1.8	1.1	1.0	1.1

Ash in Coke: 7.5%

Experimental Conditions: b) Gasification: Temperature = 950°C; Time = 12.25 hrs.
c) Impregnation with Potassium: Temperature = 1000°C; Time = 1.5 hrs.; K = 0.87%
Gasification: Temperature = 850°C; Time = 2.5 hrs.

The results obtained with powders (with particle size betwen 0.50 and 0.125 mm) from commercial coke are given in Table I. The number in the first row of part (a) is the percentage of each type of texture direct from observation. The second row is the weight of each type, on the basis of a 100 gr starting solid sample, by assuming that the density is of the same value for all textures.

From the percentage of each texture observed and the degree of burning-off, which is the weight loss of carbon, the new weight of each type of carbon is given in the second row of part (b). The weight loss percentage of each type of carbon is given in the fourth row. "Relative Micro Reactivity" (RMR) is defined by the ratio of weight loss of an individual type of carbon to the average value of the whole specimen, i.e., degree of burning-off. For the textures with RMR larger than unity, they are more reactive than the specimen as a whole. On the other hand, with RMR less than unity, they are relatively inert. For the commercial coke the isotropic, fine mosaic, granular flow and flat flow textures are very reactive and medium and coarse mosaic and creased flow are relatively inert for CO_2 oxidation.

In Table I, part (c), powders with 0.87% K were oxidized at 850°C for 2.5 hours to result in 33.4% weight loss. For the values of RMR, the

effect of potassium may be appreciated. By comparing RMR in parts (a) and (b), potassium appears to be an equalizer of RMR for all textures. It may raise reactivity of all carbon textures to give a net effect of narrowing the gap between the extreme cases. The effect is quite similar to that on macro reactivity[9].

The results obtained with coke made from low volatile coal are shown in Table II. Two basic conclusions reached for commercial coke, i.e., oxidation is selective and potassium is an equalizer, remain to be true. The creased flow carbon is the most abundant and extremely inert. The influence of potassium on the creased flow carbon in not pronounced.

Table II

Analysis of Optical Anisotropy of Coke Made from Low Volatile Coal

	% B.O.	Isotropic	Mosaic Fine	Mosaic Medium	Mosaic Coarse	Mosaic Total	Granular Flow	Flow Type Creased	Flow Type Flat	Flow Type Total
a) Before Impregnation		22.5	0.1	1.4	10.5	12.0	21.5	41.1	2.9	44.0
W (gr of C)		20.9	0.1	1.3	9.8	11.2	20.0	38.2	2.7	40.9
b) After Gasification	23.32	11.4	--	1.1	13.1	14.2	18.5	53.5	2.4	55.9
Carbon (gr)		7.9	---	0.8	9.1	9.9	12.9	37.2	1.7	38.9
ΔW=(W-Carbon)		13.0	0.1	0.5	0.7	1.3	7.1	1.0	1.0	2.0
A=(ΔW/W) %		62.2	100.0	38.5	7.1	11.6	35.5	2.6	37.0	4.9
A/% B.O.		2.7	4.3	1.7	0.3	0.5	1.5	0.1	1.6	0.2
c) After Impregnation and Gasification	22.65	12.0	---	1.0	12.1	13.1	21.6	52.3	0.8	53.1
Carbon (gr)		8.4	---	0.7	8.5	9.2	15.2	36.7	0.6	37.3
ΔW=(W-Carbon)		12.5	0.1	0.6	1.3	2.0	4.8	1.5	2.1	3.6
A=(ΔW/W) %		59.8	100.0	46.2	13.3	17.9	24.0	3.9	77.8	8.8
A/% B.O.		2.6	4.4	2.0	0.6	0.8	1.1	0.2	3.4	0.4

Ash in Coke = 7.1%
Experimental Conditions: b) Gasification: Temperature = 950°C; Time = 12 hrs.
c) Impregnation with Potassium: Temperature = 1000°C; Time = 1.5 hrs.; K = 0.67%
Gasification: Temperature = 850°C; Time = 2.75 hrs.

In Table III, results with coke from high volatile coal are listed. The oxidation is very strongly selective. The medium mosaic is the most abundant and extremely inert. The negative values of weight loss have no physical meaning, but the indication of the lack of accuracy of the measurement. The catalytic effect appears to be strong with fine mosaic and not noticeable at all for the very inert structure, the medium mosaic.

In the literature, only the laboratory results[4] are reported with the degree of burning-off, so that the Relative Micro Reactivity can be computed, as shown in Table IV. There is no obvious trend that could be visualized. It may be due to the experimental conditions that the kinetics

of carbon oxidation may be dominated by mass transfer rather than by the properties of the solids.

Table III

Analysis of Optical Anisotropy of a Coke Made From High Volatile Coal

	% B.O.	Isotropic	Mosaic Fine	Mosaic Medium	Mosaic Coarse	Mosaic Total	Granular Flow	Flow Type Creased	Flow Type Flat	Total
a) Before Impregnation		15.3	22.5	57.5	3.0	83.0	1.2	0.5	---	0.5
W (gr. of C)		14.2	20.9	53.3	2.8	77.0	1.1	0.5	---	0.5
b) After Gasification	21.44	4.0	6.0	81.8	5.9	93.7	2.3	---	---	---
Carbon (gr)		2.9	4.3	58.3	4.2	66.8	1.6	---	---	---
ΔW = (W-Carbon)		11.3	16.6	−5.0	−1.4	10.2	−0.5	0.5	---	0.5
A = (ΔW/W) (%)		79.6	79.4			13.2		100.0		100.0
A/% B.O. = RMR		3.7	3.7			0.6		4.7	---	4.7
c) After Impregnation and Gasification	19.06	6.0	2.3	84.3	5.1	91.7	2.1	0.2	---	0.2
Carbon (gr)		4.4	1.7	62.1	3.8	67.5	1.5	0.1	---	0.1
ΔW = (W-Carbon)		9.8	19.2	−8.8	−1.0	9.5	−0.4	0.4	---	0.4
A = (ΔW/W) (%)		69.0	91.9			12.3		80.0	---	80.0
A/% B.O. = RMR		3.6	4.8			0.6		4.2		4.2

Ash in Coke: = 7.3%
Experimental Conditions: b) Gasification: Temperature = 950°C; Time = 7.5 hrs.
c) Impregnation with Potassium: Temperature = 1000°C; Time = 1.5 hrs.; K = 0.41%
Gasification: Temperature = 850°C; Time = 4 hrs.

Table IV

Relative Micro Reactivity Computed from Data in Table I of Ref.

% B.O.	Isotropic	Mosaic Fine	Mosaic Coarse	Mosaic Total	Flow Type Fibrous	Flow Type Leaflet	Fragment	Fusite-like
20	2.7	1.3	0.9	1.2		1.1	0.1	1.3
30	1.8	1.8	1.1	1.6			0.8	1.3
40	1.6	1.2		0.8	1.0	0.4	0.7	2.1
50	1.7	1.2	0.7	1.0	0.5	0.4	0.6	1.7
60	1.6	1.5		1.0	1.4	1.1	0.1	1.6

Table V
Kinetics of Oxidation of Coke Powders

	Commercial	HV	LV
Temp. = 950°C			
Weight Loss (ΔW) (%)	18.65	21.44	23.32
Reaction time (hr)	12.25	7.5	12.00
ΔW/Time (%/hr)	1.52	2.85	1.94
Temp. = 850°C			
Potassium (%)	0.87	0.41	0.67
ΔW (%)	33.4	19.05	22.65
t (hr)	2.5	4.0	2.75
ΔW/t (%/hr)	13.36	4.76	8.24

Kinetics of Oxidation of Coke Powders

The results are shown in Table V. Without potassium impregnation, coke from a high volatile coal is the most reactive and commercial coke the least. The order is erversed after the exposure to Ar-K mixtures under identical conditions. Coke from HV has more than half (57%) in the very inert form, medium mosaic, with respect to CO_2 attack. It may also be responsible for the lower rate of potassium pick-up.

From the very limited data shown in Table V, one may reach a preliminary conclusion that coke reactivities with respect to solution loss-reaction and potassium absorption, are not necessarily related. The amount of potassium in the coke, at the level shown in the table, seems to be more important than the reactivity prior to impregnation in the determination of the final reactivity.

C. Conclusions

(1) Coke absorbs alkali vapors from gaseous phase to form intercalation compounds to weaken its strength. It may cause degradation of coke in the stack of the blast furnace without involving gasification of carbon.

(2) The catalytic effect of alkalies promotes solution loss reaction at a lower temperature and at a faster rate.

(3) When the degree of burning-off is low (< 20%), the main mechanism for the weakening of coke is the cracking due to intercalation compounds. At a higher degree of burning-off (> 20%), gasification of carbon is the main cause for the degradation of coke.

(4) The new index, "Relative Micro Reactivity" (RMR) has been defined to illustrate the relative easiness for carbon of the various types of textures to be oxidized by CO_2.

(5) The preliminary microscopic analysis of partially oxidized specimens of three types of coke lead to the following conclusions:

(a) Oxidation of carbon is definitely selective at least at lower temperatures.

(b) The absorption of potassium by carbon could also be selective, but in a different manner.

(6) A better control of the texture of carbon in the blast furnace coke could lead to drastic improvement in its resistance to the attack by carbon dioxide and alkali vapors.

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